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CITATION:

Osugi, Jiro ...[et al]. Optical studies of pressure effects : III. Pressure effect on the aqueous solution of amylose-iodine complex. The Review of Physical Chemistry of Japan 1967, 36(2): 88-92

ISSUE DATE:

1967-04-30

URL:

<http://hdl.handle.net/2433/46885>

RIGHT:

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 36, NO. 2, 1966

OPTICAL STUDIES OF PRESSURE EFFECTS

III Pressure Effect on the Aqueous Solution of Amylose-iodine Complex

BY JIRO OSUGI AND YOICHI KITAMURA

The absorption spectrum of an aqueous solution of amylose-iodine complex was measured under high pressure up to 4000 kg/cm².

The absorption intensity at 620 m μ decreases with increase of pressure and the intensity does not return to its initial value at normal pressure.

It is not reasonable to regard this change as induced by the transition from helix to random-coil configuration of amylose molecules, judging from the result concerning the viscosity change and the pressure effect on the solution containing only amylose.

It may be considered qualitatively that this change is due to the shift of the equilibrium between free I₂ and I₃⁻ in the complex solution under high pressure.

Introduction

It is known since the early 19th century that a blue complex is formed between amylose and iodine. This complex was investigated by R. E. Rundle.

From X-ray diffraction studies,¹⁾ he proposed a helical configuration of the amylose molecule with iodine molecules occupying the helix interior for solid complex. By the method of flow dichroism,²⁾ he also suggested the analogous structure for the complex in an aqueous solution.

Later, it was found by S. Ono³⁾ that the viscosity change due to the amylose molecules in a mixed solvent of water and dimethylsulfoxide is suddenly caused at the water content which is necessary for complex formation, and he pointed out the necessity of helical configuration of the amylose molecule for complex formation.

Theoretically, this structure of the complex is also supported by the considerations that the dipole interaction⁴⁾ between the amylose molecule and the iodine molecules in the helix stabilizes the complex and that the absorption maximum near 620 m μ can be well predicted by treating it as a charge transfer complex.⁵⁾

However, the nature of an aqueous solution of the complex is much influenced by the tempera-

(Received February 10, 1967)

1) R. E. Rundle, *J. Am. Chem. Soc.*, **65**, 1707 (1943)

2) R. E. Rundle, *J. Am. Chem. Soc.*, **65**, 554 (1943)

3) S. Ono and T. Watanabe, *Bull. Chem. Soc. Japan*, **38**, 643 (1965)

4) R. E. Rundle, *J. Chem. Phys.*, **16**, 195 (1948)

5) H. Murakami, *J. Chem. Phys.*, **22**, 367 (1954)

ture,⁶⁾ the concentration of coexisting salts,⁷⁾ and other agencies. The mechanisms of these phenomena are not fully understood. In the following experiments, the present authors attempt to obtain some informations concerning the character of the aqueous solution of the complex by means of the measurement of the absorption spectrum under high pressure up to 4000 kg/cm².

Experimentals

The high pressure bomb for spectroscopic measurements is the same as used in the previous investigation⁸⁾ and is not shown here. To avoid the influence of the material for the pressure bomb, the sample is put in a syringe, which is surrounded with liquid paraffin as a pressure transmitting medium. So, the path length of the sample is not accurately determined. It is about 5 mm.

The amylose material was kindly supplied by Professor S. Ono of Prefectural University of Osaka. The number-average molecular weight of this sample was of an order of 10⁵. The complex solution was prepared by the following procedures.

- i) 3 mg of I₂ and 18.7 mg of KI were dissolved in 100 ml of water and stirred for about 24 hrs. Then this solution was 4-fold diluted.
- ii) 15.3 mg of amylose was dispersed in 25 ml of 0.5 N-KOH aqueous solution and stirred for several hrs. After standing for about a day to complete the dissolution, this solution was neutralized to pH. 5, adding 0.5 N-HCl aqueous solution. Then, this solution was 5-fold diluted.
- iii) Each 2.5 ml of the solutions obtained by the procedures i) and ii) was mixed together.

The measurement of the absorption spectrum under high pressure was carried out as follows.

- i) The values of optical density were read with a certain slit width at each wave length and at each pressure in the case that there was only water in the syringe.
- ii) With the sample solution in the syringe, the value of optical density was read in the same way as procedure i).

The value obtained in procedure i) was subtracted from the value obtained in this procedure.

- iii) The value thus obtained was calibrated for the volume contraction of the whole sample under high pressure.

An Ostwald viscometer was used for viscosity measurements.

Results

The absorption spectra under high pressure are shown in Fig. 1. It is evident that the absorption due to the blue complex decreases with increase of pressure.

Fig. 2. shows a spectrum at normal pressure of the sample which has been compressed at a certain

6) S. Ono and T. Kuge, *Bull. Chem. Soc. Japan*, **33**, 1273 (1960)

7) S. Ono and T. Kuge, *Bull. Chem. Soc. Japan*, **33**, 1269 (1960)

8) J. Osugi and Y. Kitamura, *This Journal*, **35**, 25 (1965)

time interval. The absorption intensity once decreased at high pressure does not return to its initial value. Although the extent of this residual effect is not the same even after compression to the same pressure at the same time interval, the mean values are slightly influenced by the value of the maximum pressure and the time interval as shown in Table 1. It is noteworthy that nearly the same effect is obtained only in the case of a pressure of 1000 kg/cm² for 15 minutes as in the case of a pressure of 3000 kg/cm² for 120 minutes.

The viscosity of these samples which had shown residual pressure effect was measured. The values were the same as those which were not compressed at all.

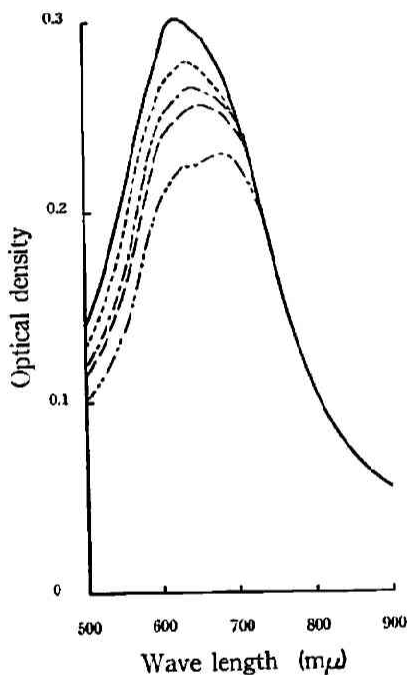


Fig. 1 The absorption spectra of an aqueous solution of amylose-iodine complex under high pressure
path length: about 5 mm
temperature: about 22°C
Made by mixing 2.5 ml of $6.6 \times 10^{-3}\%$ amylose solution with 2.5 ml of iodine-iodide solution containing 2.0×10^{-5} mole/l iodine

————— 1 kg/cm ²	----- 3000 kg/cm ²
..... 1000 kg/cm ² 4000 kg/cm ²
..... 2000 kg/cm ²	

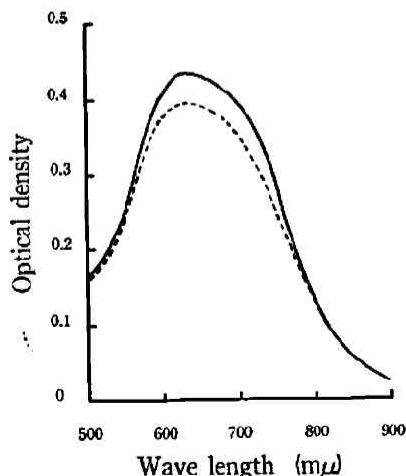


Fig. 2 The spectrum at normal pressure of the complex solution which has been compressed
path length: 10 mm
temperature: about 22°C
Made by mixing 2.5 ml of $8.4 \times 10^{-3}\%$ amylose solution with 2.5 ml of iodine-iodide solution containing 2.15×10^{-5} mole/l iodine

————— not compressed
..... compressed to 2000 kg/cm ² for 120 minutes

Optical Studies of Pressure Effects III

91

Table 1 The ratio at normal pressure of the optical density at $620\text{ m}\mu$ of the complex solution compressed to that of a complex solution not compressed

Time (min) \ Pressure (kg/cm ²)	1000	2000	3000
15	0.89		
90			0.86
120	0.90	0.89	0.86

The spectrum of the complex solution at normal pressure made by mixing an iodine solution with an amylose solution that has been compressed at a certain time interval is shown in Fig. 3.

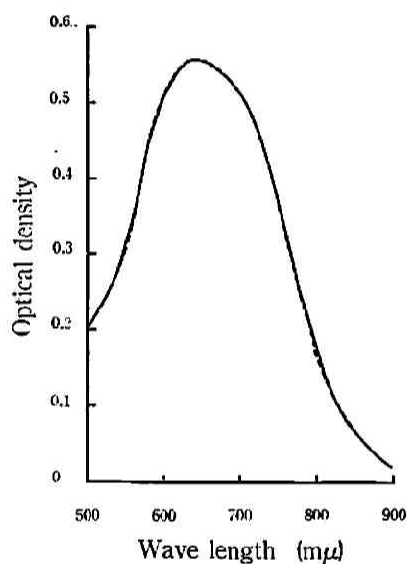


Fig. 3. The spectrum of the complex solution made from amylose solution compressed
 path length: 10 mm
 temperature: about 22°C
 Made by mixing 2.5 ml of $9 \times 10^{-3}\%$ amylose solution with 2.5 ml of iodine-iodide solution containing 2.0×10^{-5} mole/l iodine
 — not compressed
 compressed to 2000 kg/cm^2 for 180 minutes

There can be detected no change at all in comparison with the spectrum of a solution without any compression.

Discussion

From the data cited above, it is evident that pressure causes some changes in the complex, and this remains to some extents at normal pressure.

The transition from helical configuration of the amylose molecule to random one is known to be associated with the temperature change. Some change in viscosity may be accompanied with this transition as pointed out by S. Ono.³⁵ Moreover, the same pressure effect should be expected in the case of the compression of the amylose solution without any iodine.

According to our results, however, there can be detected neither change in viscosity, nor pressure effects on amylose solution without iodine. Thus it is not reasonable to consider that the pressure

effect on the complex solution is induced by the transition from helix to random configuration of the amylose molecule.

Another conceivable cause for the pressure effect is the shift of the equilibrium between free iodine and iodine in the complex.

It is known that there is an equilibrium between I_2 and I_3^- in an aqueous solution of I_2 and KI.

S. D. Hamann⁹⁾ investigated the pressure effect on the equilibrium up to 1500 kg/cm² and found that the pressure favors the concentration of I_3^- . We also followed this equilibrium up to 4000 kg/cm² and confirmed that the concentration of I_3^- linearly increases with increase of pressure as is shown in Fig. 4.

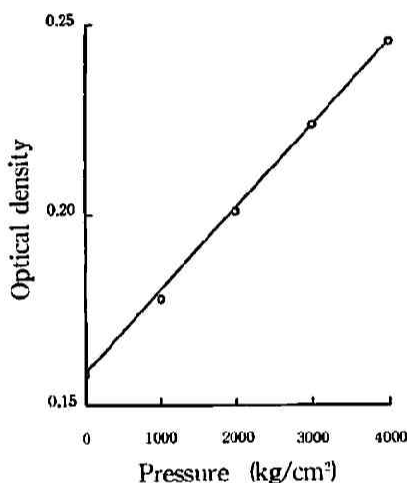


Fig. 4 The optical density at 353 m μ of an iodine-iodide solution under high pressure
 path length: about 5 mm
 temperature: about 22°C
 concentration of I_3^- : 0.134×10^{-4} mole/l
 concentration of I_2 : 0.311×10^{-4} mole/l

Thus, in the complex solution, the equilibrium between free iodine and free triiodide ion may shift to favor triiodide ion concentration under high pressure, inducing the iodine in the complex to become free iodine. Consequently the absorption by the blue complex decreases. However, a shift of an equilibrium of this kind is expected to be reversible. The pressure effect found in our experiments may be concerned with other factors such as the interaction with surrounding water molecules.

The authors have great pleasure in expressing their thanks to Professor Sozaburo Ono of Prefectural University of Osaka who has kindly supplied the amylose material and given us very useful advice throughout these experiments.

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⁹⁾ S. D. Hamann and A. H. Ewald, *Austral. J. Chem.*, 9, 54 (1956)